FORMATION OF ALUMINIUM NITRIDE

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INTRODUCTION.

The world depends upon the saltpetre fields of Chile for the ammonia formed in the destructive distillation of coal for its combined nitrogen. The nitre fields of Chile exported 1,000 tons in 1830 and reached a maximum in 1918, during the World War, when 3,250,000 tons were exported. At this rate, it is estimated that the Chilean fields will be exhausted in from twenty to fifty years. The present production of 1,500,000 tons per year by the destructive distillation of coal will probably increase rapidly as coke is being more commonly used than coal.

The combined nitrogen is used for both industrial and agricultural purposes. The production of nitric acid and ammonia depend upon it. It is also used in agriculture as a fertilizer. With the population of the world increasing, we must produce more food and only combined nitrogen can be assimilated by plant life. Atmospheric nitrogen is useless to plant

life. There is a vast field in the agricultural industry for combined nitrogen.

Owing to the increased demand for combined nitrogen and the decrease in the supply, the world seeks relief by other methods of production. The atmosphere contains approximately 80% of nitrogen by volume. On the estimation that every square mile of the earth's surface supports 20,000,000 tons, the entire atmosphere contains 4,000,000,000,000,000 tons of nitrogen. Thus, we see that we have an unlimited supply of nitrogen gas which is useless in that state, but which when combined would be of economic importance.

In recent years a great deal of work has been done on the conversion of atmospheric nitrogen into nitrogen compounds. In general three main methods were used to accomplish this result. The classifications are:

(1) Conversion of nitrogen into nitric or nitrous acids and their salts,

(2) Synthesis of ammonia and ammonium

compounds from atmospheric nitrogen, and

(3) Conversion of atmospheric nitrogen into compounds which readily yield ammonia.

The first method of fixing nitrogen as nitric and nitrous acid or as their salts consists in passing air through an electric arc of very high temperature. Between 140° C. and 620° C. the resultant product consists of NO, NO_2 and air. This resultant product may be treated with water to form nitric acid, but owing to the fact that an excess of water must be used, we can never get a concentrated solution and so it is usually absorbed by alkalies under ordinary conditions of temperature and pressure. The nitrogen peroxide formed begins to dissociate at 140° C. and is completely dissociated at 620° C. according to the equation:

$$2NO_2 \longrightarrow 2NO + O_2$$

A mixture of equimolecular proportions of NO and NO_2 behave toward alkali as nitrous anhydride, N_2O_3 and on absorption yields practically pure nitrite,

$$N_2O_3 + 2NaOH \longrightarrow 2NaNO_2 + H_2O$$

By the second method, namely, the synthesis of ammonia and ammonium compounds from atmospheric nitrogen, nitrogen and hydrogen are made to react by means of the electric spark according to the equation

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

The union takes place to a limited extent unless the ammonia formed is immediately removed from the sphere of action.

The third method, namely, the conversion of atmospheric nitrogen into compounds which readily yield ammonia. This is the only method depending on the formation of a metallic nitride whichat present seems to offer prospects of technical success. Most metals, and many non-metals form nitrides to a greater or less extent from which the nitrogen can be obtained in the form of ammonia by treatment with water or alkalies. Heated magnesium readily absorbs nitrogen forming nitride according to the equation

$$6Mg + 2N_2 = 2Mg_3N_2$$

Wilson and Mehner heat a mixture of magnesia and carbon in a current of nitrogen in an electric furnace

$$3MgO + 3C + N_2 = Mg_3N_2 + 3CO$$

The oxides of other elements which form nitrides at high temperatures react similarly. Numerous methods depending on the transformation of oxides and other compounds of B, Si, Ti, and Mo into nitrides or other nitrogen compounds of these elements, and the subsequent decomposition of the nitrogen compounds by water, acies, or alkalies, have been described and patented. None of them, so far as can be ascertained, have been tried on a technical scale.

THE SERPEK PROCESS.

The Serpek Process depends on the formation of aluminum nitride from bauxite, and subsequent decomposition of the nitride with water or alkalies. The reaction is carried on in an electric furnace at a temperature of 1600 - 1800° C. through which a current of nitrogen is passed. A history of the development of the process is given by Norton, Donath and Indra, and Richards.

Prior to the reduction of aluminum oxide as the metallic base, Serpek had experimented with aluminum carbide and succeeded in forming small quantities of the nitride by passing a current of nitrogen over finely divided aluminum carbide at a temperature of 1500 - 2000° C. He found that additions of either aluminum or carbon greatly increased the reaction. Care showed that the aluminum carbide first dissociated into aluminum and carbon after which the aluminum reacts with the nitrogen as follows:

$$Al_4C_3 + \text{heat} = 4Al + 3C$$

$$4Al + 4N \longrightarrow 4AlN$$

Serpek continued his experiments using mixtures of aluminum carbide and aluminum oxide and finally found that the nitride could be formed by using aluminum oxide alone. He claimed that aluminum carbide was first formed which reacted with some of the aluminum oxide present forming aluminum and carbon monoxide, the aluminum then combining with the nitrogen forming aluminum nitride. His theory of nitride formation is expressed in the following equations:

$$2Al_2O_3 + 9C = Al_4C_3 + 6CO$$

$$Al_4C_3 + Al_2O_3 = 6Al + 3CO$$

$$6Al + 3N_2 = 6AlN$$

Through the efforts of the Badische Aniline and Soda Fabrik, the percentage of nitride formed was found to be increased by the addition of 5 - 10% of certain oxides, namely, Si, Zn, T i, Mo, V, Be, Ce, Ur, and Dr; however, silicon is the only one that may

be used to commercial advantage owing to its abundance and low cost although the others may be used if they are recovered after the reaction. Traces of SO_2 or HCl in the nitrogen are stated to be beneficial to nitride formation, this, however, is not believed to be true.

Temperature has also been found to have a marked effect upon the production of aluminum nitride, the greatest yield being obtained from 1700 - 1800° C., although theoretically the greatest yield should be obtained just below 2200° C., that being the decomposition temperature of the aluminum nitride. At present the decomposition temperature of aluminum nitride is claimed to be somewhat lower.

EXPERIMENTAL WORK.

With the idea in mind that the formation of aluminum nitride was commercially as well as experimentally possible, we set out to make the above a foregone conclusion. In order to do this it was necessary that the best quantities of raw materials, the best catalytic agent, the best temperature and time for formation, and the flow and purity of nitrogen be ascertained. To gain this knowledge it was decided to pass a stream of nitrogen over a finely divided mixture of bauxite, carbon, and the catalytic agent varying the temperature and percentage of constituents, the reaction to be carried on in an electric furnace. After this knowledge should be obtained the reaction was to be carried out on a larger scale and the process was to be made continuous.

The same electric furnace - a Hoskins carbon resistance furnace - was used in both preliminary and final operations. A graphite tube 30 inches long, $2\frac{1}{4}$ inches wide and 1/4 inch

thick, resting on two sets of transite rollers, formed the core and reaction chamber of the furnace. Concentrically around this was the heating element of the furnace, 24 inches in length, consisting of a series of carbon plates each 3/16 inch thick, 3 inches internal diameter, and 5 inches outer diameter, fastened at one end to a stationary terminal, the other terminal being movable in order that the pressure on the plates could be adjusted, thereby varying the resistance. Two carborundum cylinders jacketed these carbon plates, which in turn were jacketed by insulating material. The outer shell of the furnace, 12 inches in diameter was made of sheet iron and was also insulated from the outer carborundum cylinder by insulating material.

In determining the preliminary information-that is, the best conditions for nitride formation, it was not necessary that the reaction chamber be revolved. After two grams of the finely divided mixture of raw materials was placed in a carbon boat which was then inserted

in the reaction chamber which had been raised to temperature. The ends of the chamber were then closed and a stream of nitrogen passed over the carbon boat containing the raw material. The reaction was allowed to continue for fifteen minutes after which the boat was removed and contents analyzed for the percentage of nitrogen by the Kjeldahl method.

After the best conditions for the formation of aluminum nitride had been ascertained the furnace was inclined to an angle of 20° and the reaction chamber converted into a rotary drum by clamping a split pulley on one end. By means of a rheostat and a series of pulleys the rotary speed of the chamber could be varied at will. The raw material which was fed into the chamber by means of a spiral conveyor, works its way down the tube against a brisk current of nitrogen and was discharged through an opening at the opposite end. The product of reaction was then analyzed as before.

RESULTS.

The raw materials consisted of a bauxite analyzing 98% Al_2O_3 and 2% Si, wood charcoal ground to 100 mesh, and the catalyzer. The amount of bauxite and carbon used in our mixtures was in theoretical proportion - 100 parts bauxite to 35.3 parts carbon - as calculated from the following equation: $Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO$.

The oxides of iron, silicon, and zirconium were experimented with as catalytic agents. The first runs did not meet with much success which we discovered was due to too slow a stream of nitrogen. On increasing the nitrogen pressure and maintaining a temperature of 1600 - 1800° C. we secured the following results using iron as the catalyzer.

% Fe_2O_3	% N
0	19.50
0	25.00
1	26.86
1	28.70
3	26.00
3	28.01
3	28.89
5	25.52

Results using zirconium oxide as the catalytic agent are given below:

% ZrO	% N
1	28.21
1	26.60
3	26.31
3	25.30
5	21.61
5	29.60
10	23.56
10	24.30

Results using silicon dioxide are given below:

% SiO_2	% N
1	27.38
1	28.74
3	26.17
3	30.18
5	21.09
5	26.70
10	27.34
10	26.98

From this data it was decided that a 3% SiO_2 mixture makes the best charge and was consequently used in our work with the revolving furnace. Our time limit enabled us to secure only three runs with the revolving furnace. None of these runs gave a product, which on analysis, showed an appreciable amount of nitrogen present.

CONCLUSION.

As a result of our investigation we may state that proper amounts of the oxides or iron, silicon, and zirconium may act as a catalytic agent in the formation of aluminum nitride. The proper amount of the catalytic agent is from 3 - 5 per cent of our best runs, containing more than 30 per cent nitrogen were made with this amount of silica present. We also find that a slight nitrogen pressure was advantageous to the reaction.

Our work with the revolving chamber showed that the nitrogen pressure was absolutely necessary. The failure of our method was due to the fact that the partial pressure of the carbon monoxide was too large in comparison with the partial pressure of the nitrogen and in accordance with the law of mass action, the presence of too much carbon dioxide caused the reaction to reverse itself to one of oxidation instead of reduction. This perhaps could have been partially remedied by having a larger exit for the escaping gases of the reaction. Another

method is to reduce the bauxite to aluminum carbide before feeding it into the reaction tube.

Another thing that might aid in the production is in having a longer reaction chamber so that the material can be raised to the proper temperature.